SOLID PHASE EXTRACTION OF TRACE AMOUNTS OF PALLADIUM IONS USING MULTIWALLED CARBON NANOTUBE MODIFIED BY N,N'-BIS (2-HYDROXY-BENZYLIDENE)-2,2'(AMINOPHENYLTHIO) ETHANE PRIOR TO DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT. Multiwalled carbon nanotubes modified with N,N'-bis(2-hydroxybenzylidene)-2,2'(aminophenylthio) ethane have been developed for the selective separation and/or preconcentration of trace amounts of Pd(II) in aqueous medium. Parameters including pH of aqueous solution, flow rates, the amount of ligand and the type of stripping solvents were optimized. It was found that the sorption is quantitative in the pH range (1.5-4), whereas quantitative desorption occurs instantaneously with 3.0 mL of 0.3 M Na_2SO_3. Linearity was maintained between 0.01 to 22 $\mu g\ mL^{-1}$ for Pd in the final solution. The breakthrough volume was greater than 1800 mL with an enrichment factor of more than 600 and 6.0 $\mu g\ L^{-1}$ detection limit (3s, n = 10). The effects of various ions interferences on the percent recovery of palladium ion were studied. The method was successfully applied to the determination of palladium ion in environmental samples.

KEY WORDS: Multiwalled carbon nanotubes, Preconcentration, Palladium(II) determination

INTRODUCTION

Palladium is a metal of economic importance due to its extensive use in metallurgy, in various chemical syntheses, production of dental and medicinal devices and in jewellery manufacture [1]. This metal may enter the environment and interact with complexing materials, such as humic substances [2]. Palladium has no biological role and all palladium compounds should be regarded as highly toxic and carcinogenic. However, palladium chloride was formerly prescribed as a treatment for tuberculosis without too many bad side effects. There is currently much discussion about its bioavailability and toxicology [3]. Thus, due to its increasing use, on the one hand, and the toxicity of Pd(II) compounds to mammals, fish and higher plants, on the other hand, the separation and determination of palladium is of special interest in environmental analysis. Low concentration of Pd in industrial ($\mu g\ g^{-1}$ level) and environmental samples (ng g^{-1} level) together with the complexity of the matrix cause much interference during the determination of palladium. Therefore, the application of highly sensitive techniques, such as flame atomic absorption spectrometry (FAAS) [4, 5], graphite furnace atomic absorption spectrometry (GFAAS) [6, 7], inductively coupled plasma-atomic emission spectrometry ICP-AES [8, 9], inductively coupled plasma mass spectrometry ICP-MS [10, 11], coupled with a separation and enrichment procedure is necessary [12-14].

Typically, solid-phase extraction (SPE) replaces liquid-liquid extraction as a sample preparation tool and provides a method that is simple and safe to use. The benefits of SPE include high recoveries of analytes, purified extracts, high preconcentration factors, ease of automation, and reduction in the consumption of organic solvents [15, 16]. The methods for producing solid phase material for SPE include binding the metal ion with chelating agents and adsorption on a solid phase such as octadecylsilane [17, 18], and using chemically bonded silica gel [19, 20], activated carbon [21, 22], ion-exchange resins [23, 24], chelating resins [25, 26], zeolites [27-29] and various polymers [30].

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    Recently, carbon nanotubes (CNTs) [31, 32] have been used for the extraction and analysis of many different organic and environmental matrices. Moreover, these sorbents modified by suitable ligands, are successfully used for the separation and sensitive determination of metal ions [32-36]. In general, Schiff ligands are among the oldest ligands in coordination chemistry [37]. The Schiff bases derived from salicylaldehyde (salen) as polydentate ligands are known to form very stable complexes with transition metal ions [38, 39].

    In the present investigation, the analytical potential of multiwalled carbon nanotubes (MWCNTs) modified with N,N'-bis(2-hydroxybenzylidene)-2,2'(aminophenylthio) ethane (NBHAE) (Figure 1) was examined for preconcentration of Pd(II) in aqueous samples prior to its flame atomic absorption spectrometric determination. The analytical conditions for the preconcentration (quantitative retentions) of analyte were investigated.
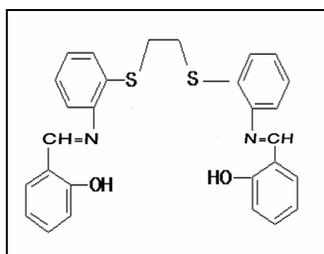

Figure 1. Structure of N,N`-bis(2-hydroxybenzylidene)-2,2`(aminophenylthio) ethane (NBHAE).

EXPERIMENTAL

Apparatus

The palladium measurement was performed with a Varian Spectr AA220 atomic absorption spectrometer (Australia) equipped with a computer processor. A palladium hollow cathode lamp, operated at 5 mA, was utilized as the radiation source. The analytical wavelength (363.5 nm) and slit width (0.1 nm) were used as recommended by manufacturers. The pH values were measured with a metrohm 827 pH meter (Herisau, Switzerland) supplied with a combined glass electrode. A funnel-tipped glass tube (80×5 mm) was used as column for preconcentration. All glassware and columns were washed with mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before use.

Reagents and materials

All the reagents used were of the highest purity available and at least of analytical reagent grade. The stock solution of Pd(II) (100 µg mL^{-1}) was prepared by dissolving the proper amount of Pd(CH$_3$COO)$_2$ from Merck (Darmstadt, Germany) in 2 mol L^{-1} hydrochloric acid solution. Standard solutions of Pd(II) were prepared daily by appropriate dilution of palladium stock solution. Stock solution of diverse elements was prepared from high purity compounds. Multiwalled carbon nanotubes of 95% purity and length 1-10 µm, number of walls 3-15 were purchased from Plasma Chem. GmbH (Germany). The Schiff base ligand NBHAE was synthesized and purified as reported in the literature [40]. A 0.2% (m/v) solution of NBHAE was prepared by dissolving of 50 mg of NBHAE in 1.0 mL of DMF and diluting to 25.0 mL with ethanol.

Preparation of modified MWCNTs

Prior to use, MWCNTs materials were oxidized with concentrated HNO_3 according to literature with minor modification [32]. In order to create binding sites onto the surface, 3.0 g of MWCNTs were first soaked in 30 mL of concentration HNO_3 for 12 h at room temperature while being stirred [41]. Then the solution was filtered through a 0.45 μm membrane filter and the MWCNTs were washed with distilled water until the pH was neutral. 2 g of MWCNTs was suspended in 20 mL 0.2% (m/v) solution of NBHAE and the mixture was refluxed with stirring for 4 h. The solid was filtered, washed with water and dried at 80 °C. The amount of NBHAE deposited on the MWCNTs was estimated by spectrometric measurements from the residual amount of NBHAE in solution.

Column preparation

An aliquot 40.0 mg of modified MWCNTs was slurred in water, and then poured into a funnel-tipped glass tube (80 × 5 mm) plugged with a small portion of cotton at ends. The column could be used repeatedly after washing with distilled water.

Recommended procedure

Fifty milliliters of an aqueous solution containing 5.0 μg of Pd(II) was taken and the pH was adjusted to about 2. The resulting solution was passed through the column at flow rate of about 1 mL min^{-1}. After passing of solution completely, the column was rinsed with 5 mL of water and the adsorbed ions were eluted with 3.0 mL 0.3 M Na_2SO_3 with a flow rate of 1 mL min^{-1}. The Pd(II) in the eluent were determined by FAAS.

RESULTS AND DISCUSSION

Some preliminary experiments were carried out in order to investigate the quantitative retention of Pd(II) ions by MWCNTs in the absence and presence of NBHAE. Experimental results showed that MWCNTs have a tendency for the retention of metal ions adsorption (<40 % for Pd^{2+}) but were not selective. Modified multiwalled carbon nanotube with NBHAE has a greater capacity of adsorption and selectivity of ions. In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as, the nature and concentration of eluent, pH of the sample solution, volume and type of the eluent solution, the flow rate of eluent and sample solutions and volume of the sample solution. Various ions interferences effects were also investigated.

Choice of eluent

One of the important factors that affect the preconcentration procedure is the type, volume and concentration of the eluent used for the removal of metal ions from the sorbent [42]. In order to choose the most effective eluent for the quantitative stripping of the retained Pd(II) ions by the modified column MWCNTs with NBHAE, after the extraction from 50 mL water (pH 2), the Pd(II) were stripped with 3 mL of various stripping agents. The results are summarized in Table 1. Results showed that the elution of the retained Pd(II) was quantitative with Na_2SO_3. The effect of varying concentration of Na_2SO_3 on the recovery of Pd(II) was also studied and the results are included in Table 1. As can be seen, 3 mL of 0.3 M Na_2SO_3 solution can accomplish the quantitative elution of Pd(II) from the modified column.

Table 1. Percent recovery of Pd(II) from the modified column as a function of stripping solutions[a].

Stripping agent	Recovery (%)[b]
HCl (0.1 M)	92.0 ± 0.5
Thiourea	89.1 ± 0.6
$Na_2S_2O_3$	86.0 ± 0.5
KSCN	64.3 ± 1.0
Na_2SO_3 (0.1 M)	98.0 ± 0.7
Na_2SO_3 (0.3 M)	99.6 ± 0.4
Na_2SO_3 (0..5 M)	99.5 ± 0.5

[a]Initial samples contained 5.0 μg Pd(II) in 50 mL water. [b]Average of four determinations ± standard deviation.

Effect of the sample pH

One of the most important parameters affecting the preconcentration procedure is the pH of the solution, because the formation of soluble metal complexes and their stabilities in aqueous solutions are strongly related to the pH of the medium [43, 44]. The influence of pH on the recovery of Pd(II) was examined in the pH range of 1-10 (Figure 2). It was found that the sorption is quantitative in the pH range (1.5-4.0). Therefore the pH was adjusted to about 2 for subsequent experiments.
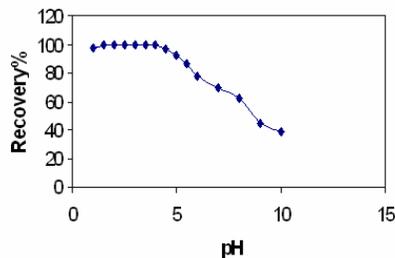

Figure 2. Effect of pH of sample solution on the recovery of Pd(II).

Effect of flow rates of sample and eluent solution

The retention of an element on an adsorbent also depends on the flow rate of the sample solution [42]. Thus, the effect of flow rates of the sample and elution solutions on the retention and recovery of ions was investigated under optimum conditions. It was found that retention and recovery of the ions was independent of flow rate in a range of 0.5-1.5 mL min^{-1}. Therefore a flow rate of 1 mL min^{-1} was applied for sample and elution solutions in all subsequent experiments.

Breakthrough volume

The measurement of breakthrough volume is important in solid-phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample [42]. The breakthrough volume is strongly dependent on the nature of both the sorbent and the trace element, as well as on the mass of sorbent considered and the analyte concentration in the sample [45]. In addition, it depends on the sorbent containers, as discs usually offer higher breakthrough volumes than cartridges. The

breakthrough volume of sample solution was tested by dissolving 5.0 μg Pd(II) in 50, 100, 500, 1000, 1500, 1800 and 2000 mL water and the recommended procedure was followed under optimal experimental conditions. In all cases to 1800 mL the extraction by the column was found to be quantitative. Thus, the breakthrough volume for the method should be greater than 1800 mL. Consequently, by considering the final elution volume of 3.0 mL and the breakthrough volume of 1800 mL, an enrichment factor of 600 was easily achievable.

Adsorption capacity

The adsorption capacity is the maximum metal quantity taken up by 1 g of solid phase and given by mg metal g^{-1} modified solid phase [46]. The adsorption capacities of modified column were determined by batch and column methods.

Batch method

Fifty milliliters of solution containing 4.0 mg of palladium at pH 2 was added to 40.0 mg sorbent. After shaking for 30 min, the mixture was filtered. A 10.0 mL aliquot of the supernatant solution was diluted to 100.0 mL and determined by FAAS. The capacity of sorbent for Pd(II) was found 86 mg g^{-1}.

Column method

In addition the sorption capacity of the column was determined by passing 40.0 mL of 100.0 μg mL^{-1} of Pd(II) at pH 2 through the column, followed by the determination of the retained ions using atomic absorption spectrometry. The maximum capacity of the sorbent for Pd(II) was found 98 mg g^{-1}.

Analytical performance

Calibration curve was constructed for the determination of Pd(II) according to the general procedure under the optimized conditions. Linearity was maintained between 0.01-22.0 μg mL^{-1} in the final solution with a correlation factor of 0.9999 (A = 0.0446 C + 0.0308). The limits of detection (LOD) based on three times the standard deviation of the blank ($3S_b$) [47] under optimal experimental conditions was 6.0 μg L^{-1} (n = 10). The reproducibility of the proposed method for the extraction and determination of 5.0 mg of Pd(II) from 50 mL of water was also studied. The obtained RSD in 10 replicate measurements was 2.43%.

Matrix effects

Matrix effects are important problem in the determination of metals in real samples [48, 49]. In order to assess the possible analytical applications of the recommended procedure, the interference due to several cations and anions was examined under optimized conditions. For these studies an aliquot of aqueous solution (50 mL) containing 5.0 μg of Pd(II) was taken with different amounts of foreign ions and the procedure was implemented. The tolerance limit was defined as the highest amount of foreign ions that produced an error no greater than ±3% in the determination of investigated palladium ions. The results are summarized in Table 2. The results show that the proposed method is selective and can be used for determination of Pd(II) in various samples without interference.

Table 2. Effect of interfering ions[a].

Coexisting ions	Ion concentration/Pd concentration	Coexisting ions	Ion concentration/Pd concentration
Mg^{2+}, Ca^{2+}	4000	ClO_4^-	2150
Na^+, NH_4^+, K^+	5000[b]	Cd(II)	1100
CH_3COO^-, NO_3^-	5000[b]	Pb(II)	890
EDTA	500	Zn(II)	800
Tartrate	650	Co(II)	600
Oxalate	700	Rh(III)	740
$H_2PO_4^-$	2500	Mn(II)	250
HPO_4^{-2}	3000	Au(III)	150
SO_4^{2-}	2550	Cu(II)	770
CO_3^{2-}	2050	Ni(II)	820
PO_4^{3-}	2350	Fe(III)	950

[a]*Conditions:* Initial samples contained 5.0 μg Pd^{2+} and different amounts of various ions in 50 mL water. [b]Above which was not tested.

Accuracy and applications

In order to assess the applicability of the method to real samples with different matrices containing varying amount of a variety of diverse ions it was applied to the separation and recovery of Pd(II) ions from two different synthetic and three water samples. According to the results, the concentration of Pd(II) in analyzed water samples was below the LOD of the method. The suitability of the proposed method for the analysis of water samples was checked by spiking samples with 5.0 and 10.0 μg mL^{-1} of Pd(II). Good recoveries (96-102%) were achieved for all analyzed samples. The data obtained with the proposed method were presented in Table 3. The results indicate that the proposed method can be reliably used for the determination of palladium in various matrices.

Table 3. Determination of Pd(II) in water and synthetic samples.

Sample	Spiked (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Well water (Shahid Bahonar University)	-	N.D [b]	-
	10.0	9.9 ± 0.2	99
	5.0	4.8 ± 0.1	96
Tap water (Kerman drinking water)	-	N.D	-
	10.0	9.8 ± 0.2	98
	5.0	4.9± 0.3	98
Synthetic sample 1[c]	5.0	4.9 ± 0.1	98
Synthetic sample 2[d]	5.0	5.1 ± 0.3	102

[a]Average of four determinations ±standard deviation. [b]Not detected. [c]Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Ba^{2+}, Fe^{3+}, Hg^{2+}, Co^{2+}, Cu^{2+}, 1 mg of each cation. [d]Mg^{2+}, Ca^{2+}, Na^+, NH_4^+, K^+, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Ba^{2+}, Fe^{3+}, Hg^{2+}, Co^{2+}, Cu^{2+}, 3 mg of each cation.

Comparison of this method with other methods

Several methods have been reported in the literature for the preconcentration and determination of palladium. Some characteristics of previously reported methods such as enrichment factor and LOD are summarized in Table 4 for comparison. As can be seen, the proposed SPE method in this work, for the preconcentration of Pd(II), shows a high enrichment factor to the previously reported methods. In addition, its low cost and simplicity as well as its high selectivity for Pd(II)

make it as a suitable quantitative determination method. The method was successfully applied to the determination of trace amount of palladium in water samples with excellent recoveries.

Table 4. Comparison of the published preconcentration methods for Pd with the proposed method.

Preconcentration method	Determination method	Enrichment factor	Detection limit ($\mu g\ L^{-1}$)	Linear range ($\mu g\ L^{-1}$)	Reference
SPE	FAAS	100	12	-	[35]
DLLME[a]	FAAS	45.7	90	100 - 2000	[50]
DLLME	GFAAS	156	0.0024	0.1 - 5	[51]
SFODME based on USD[b]	FAAS	49.9	0.60	2 - 400	[5]
SPE	FAAS	600	6.0	10-22000	This work

[a]Dispersive liquid-liquid microextraction. [b]Solidified floating organic drop microextraction based on ultrasound-dispersion.

CONCLUSIONS

Palladium can be determined successfully by using the proposed separation/preconcentration method in the presence of high concentrations of matrix ions. The proposed method is simple, precise and accurate. Recovery values obtained are in the range 96-102% which demonstrates the applicability of the method and indicates that the method is essentially free from interferences for a large number of diverse ions, which are associated with Pd in its natural occurrence and industrial samples. Due to relative high preconcentration factor, trace metal ion at ppb level can be determined by this proposed method. The use of organic solvents in the proposed method is eliminated. The reproducibility of the method is at the most 2.43%. The method is economical and during the step of desorption the ligand remains in the modified column, which allows using the column more than once.

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